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ORIGINAL PAPER

Zirconia-based matrices for actinide management in recycling LWR claddings

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Abstract

We are investigating the use of Light Water Reactor claddings as precursor materials in zirconia-based matrices for the conditioning and transmutation/burning of actinides. This study examined two un-irradiated zirconium-rich claddings: Zircaloy-4 and M5®. After complete oxidation and characterization, both materials were converted into Yttria Cubic-Stabilized-Zirconia (YSZ) and pyrochlore ($Nd_2Zr_2O_7$), with neodymium used as a surrogate for actinides. We present preliminary results and discuss a potential scenario for an innovative back-end fuel cycle.

Introduction

Nuclear waste management is a critical issue for the nuclear industry. Among the various options considered for managing transuranium elements (Np, Pu, Am, Cm), two alternatives are currently being explored: the final disposal of waste in a deep underground repository and the "burning" of nuclear waste in dedicated reactors such as Fast Reactors and Accelerator Driven Systems. Sometimes, these options are envisioned as part of a combined cycle. In considering materials for a once-through cycle concept, zirconia-based materials, such as Yttria-Stabilized Zirconia (YSZ) and zirconate pyrochlore oxides, have been proposed as matrices for radioactive waste disposal. This is due to their excellent chemical durability [1, 2], as well as their potential use as inert matrix fuels [3–9]. Both YSZ and zirconate pyrochlore exhibit outstanding resistance to alpha decay of actinides, as demonstrated in various studies [10, 11]. All actinides relevant to the present studies can form solid solutions with YSZ [9, 12], while only Pu, Am, and Cm can be incorporated in their trivalent cationic form within zirconate pyrochlore [13]. This research explores the possibility of using light water reactor (LWR) claddings as precursor materials for the synthesis of these zirconia-based ceramics.

Fuel claddings in LWRs are primarily made from zirconium-rich alloys, with zirconium content exceeding 98 wt%. For example, the Zircaloy-4 alloy consists of 1.4–1.6 wt% Sn, 0.18–0.24 wt% Fe, and 0.07–0.13 wt% Cr. A more recent alloy, known as M5, is used in European power plants operated by Framatome-ANP and contains 0.8–1.2 wt% Nb, 0.05 wt% Fe, and 0.015 wt%Cr. Each fuel assembly of the AF-2G E type, which contains 264 rods, uses approximately 125 kg of one of these alloys. This adds up to about 19.6 metric tons for a 900 MWe reactor, although the exact quantity varies depending on the reactor's type and power output. During the reprocessing of fuels, as practiced in France, these cladding materials are treated as technological waste. The reprocessing process involves chopping the cladding, washing it in hot nitric acid, rinsing it, then compacting it into disks. These disks are placed in special stainless-steel containers for disposal in a dedicated repository. Exploring the potential for reusing these cladding materials as precursor substances for burning/transmutation and conditioning of actinides could significantly minimize waste. This paper describes our preliminary investigations conducted on un-irradiated cladding elements.

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Experimental

Synthesis

Zircaloy-4 (Zry-4) and M5 cladding tubes (10.75 mm $\varnothing_{\text{out.}}$ diameter, 0.725 mm wall thickness) were provided by AREVA GmbH. Oxidation of the samples for 90 min at 1400 °C in argon/oxygen atmosphere was performed and controlled using a thermal balance NETZSCH STA 409. Once completely oxidized, samples were crushed and ground into powders in an agate mortar.

Yttria (Y_2O_3) (Alfa Aesar 99.9%) was used as stabilizing agent [14]. The YSZ compounds with composition, $(Zr_{0.7},Y_{0.3})O_{1.85}$, were prepared by mixing the appropriate amounts of polycrystalline starting materials, mixing/grinding the powders in an agate mortar with acetone and calcining the slurry in air at 1400 °C for 48 h. The operation of grinding/calcining was repeated several times until the final product was found to be single phase. A total of about 200 h at 1400 °C was necessary to obtain a pure product. The same procedure was applied to prepare the pyrochlore oxide $Nd_2Zr_2O_7$. For the latter Nd_2O_3 polycrystalline (Merck 99.99%) was used.

Characterization

The XRD data was collected at room temperature using a high-resolution Bruker D8 X-ray diffractometer mounted in a Bragg–Brentano configuration, with a curved Ge monochromator (111), a ceramic Cu X-ray tube (40 kV, 40 mA) and a Vantec position-sensitive detector. The scan was collected with 2θ ranging from 20° to 120° using 0.0086° step-intervals with counting steps of 3 s. The X-ray diffraction pattern was refined by the Rietveld method [15] using the FullProf suite [16]. The shape of the peaks was described by the Pseudo-Voigt function and the background was fitted based on linear interpolation between a set of about 30 background points with refinable heights.

To check the microstructure od the samples, SEM analysis was performed using a VEGA-TESCAN-5130-LS instrument equipped with energy and wavelength dispersive detector systems and allowing a magnification up to $\times 10^6$.

Results and discussion

At high temperatures, zirconium and its alloys react vigorously with oxygen, air and steam to form zirconia (ZrO_2) [17–20]. The corresponding enthalpy of reaction, e.g., in oxygen is $\Delta H = -1100.8 \pm 2.1$ kJ/mol [21]. Detailed mechanisms of oxidation are described in references [22, 23].

The complete oxidation of Zircaloy-4 and M5 claddings was reached after about 60 and 40 min, respectively, confirmed by 35 wt% mass gain in the thermogravimetric experiment (Fig. 1). Each tube fragment, once fully oxidized, gave a white–gray material. The fully oxidized claddings were crushed into powder and the polycrystalline material analyzed by X-ray diffraction and scanning electron microscopy (Fig. 2).

For the Zircaloy-4 cladding, the oxidized product was composed of monoclinic m-ZrO_2—($a = 0.5148$ nm,

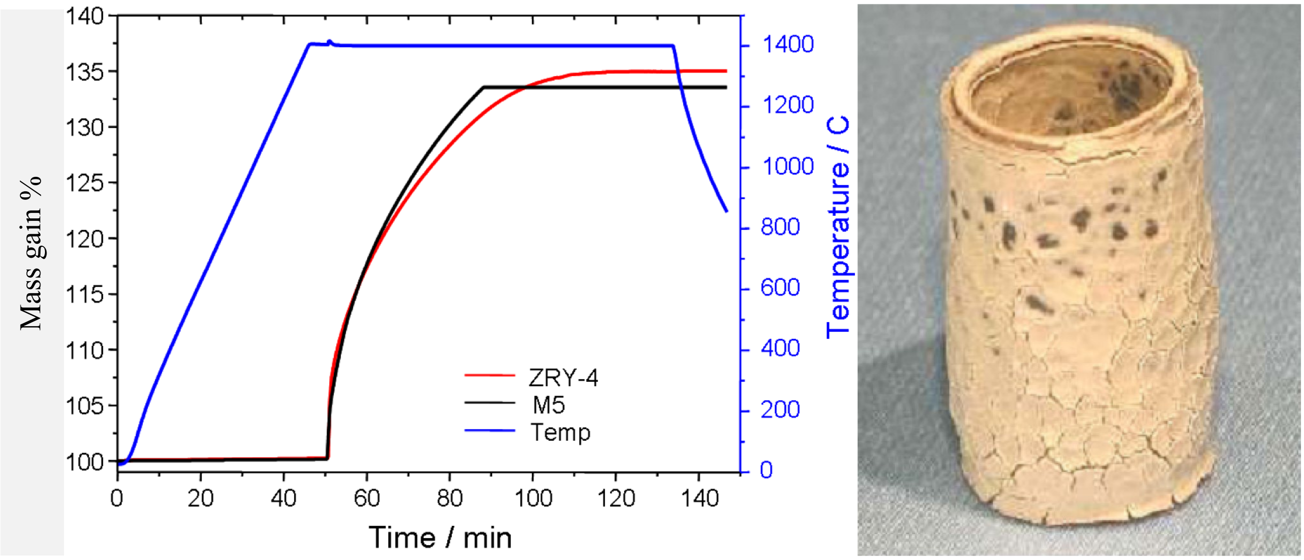

Fig. 1 Thermogravimetric curves and temperature evolution during oxidation of Zircaloy-4 and M5 cladding materials (left). Picture of fully oxidized Zircaloy-4 sample (right)

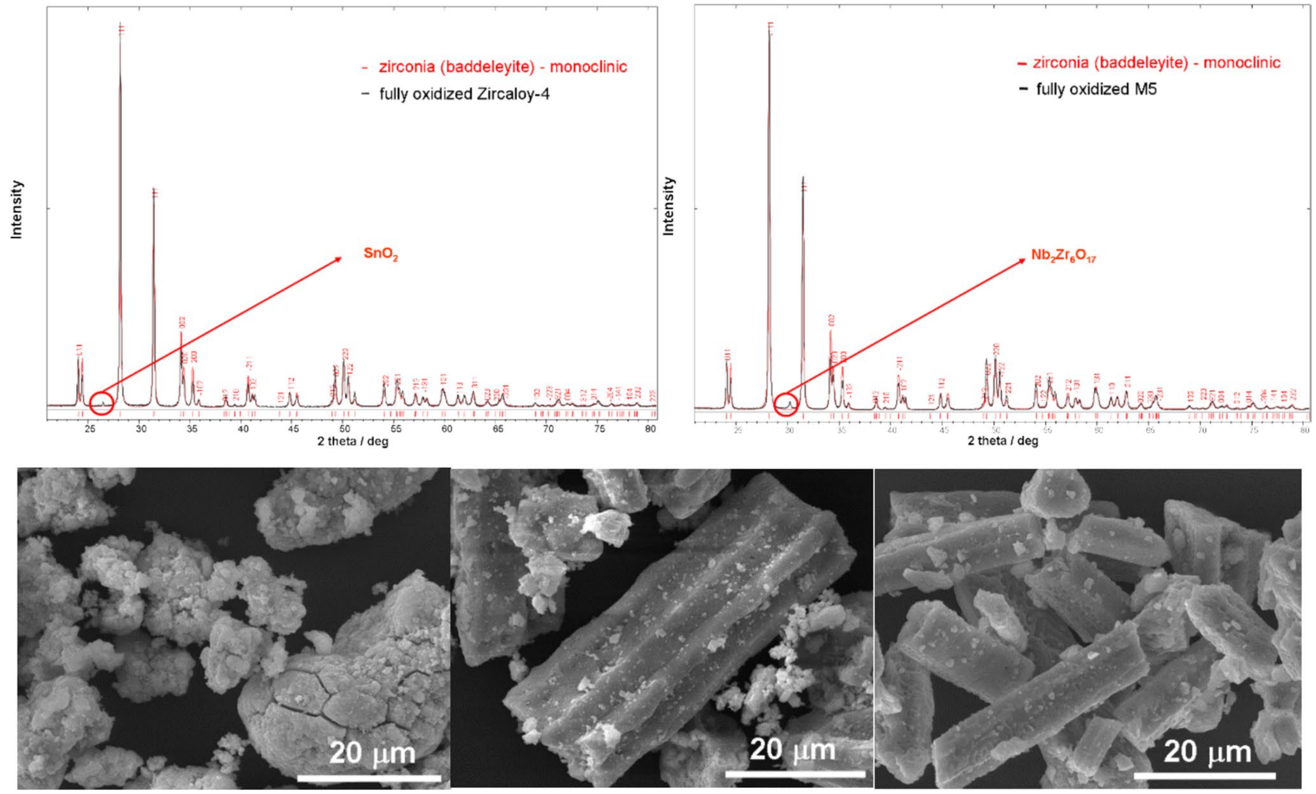

Fig. 2 Top rows: X-ray diffraction pattern of oxidized Zircaloy-4 (left) and M5 (right) alloys at 1400 °C. Bottom row: SEM micrographs of commercial *monoclinic*-ZrO$_2$ (left), Zircaloy-4 (middle) and M5 (right) after complete oxidation at 1400 °C

$b = 0.5202$ nm, $c = 0.5311$ nm, $\beta = 99.22°$) and a small amount of tetragonal SnO$_2$. For the M5 alloy, the oxidized product was composed as well of monoclinic zirconia ($a = 0.5149$ nm, $b = 0.5207$ nm, $c = 0.5313$ nm, $\beta = 99.21°$) and traces of a niobium-zirconium oxide, probably Nb$_2$Zr$_6$O$_{17}$ according to the ZrO$_2$-Nb$_2$O$_5$ phase diagram. [24] The samples were also analyzed by SEM and compared to commercial zirconia provided by Alfa Aesar 99.7%. One can notice the large grain size and the elongated "monoclinic" shape of the Zry-4 and M5 oxidized products that will increase the reaction kinetic of conversion into zirconia-based matrices. The difference in the morphology of commercial zirconia can be attributed to the chemical method used for its production, likely a sol–gel process, which involves calcination at significantly lower temperatures.

A similar approach was performed in the case of irradiated Zircaloy-4. Because of the mechanically cleaning after the irradiation process and the small quantity involved (< 5 mg), the dose rate of this sample was low (< 4–5 µSv/h) which allowed us to manipulate the sample into glovebox and to oxidize it at 1300 °C for 5 h in air. After oxidation the sample has changed its initial form and increased in weight by 33.5%. The X-ray diffraction analysis revealed that the irradiated Zircaloy-4 cladding, after undergoing oxidation, transforms into monoclinic zirconia (as depicted in Fig. 3). However, unlike the un-irradiated sample, no SnO$_2$ oxide was detected, likely due to the significant gamma background observed at low angles.

To demonstrate the conversion of zirconia into the potential matrices for conditioning of actinides, we have used the un-irradiated claddings. Two types of crystalline ceramic materials, both derivatives from the fluorite structure, have attracted our attention: YSZ and pyrochlore Nd$_2$Zr$_2$O$_7$.

For preparation of yttria-stabilized samples, the oxidized claddings were mixed with 17.65 mol% of Y$_2$O$_3$ and calcined at 1500 °C. A fully cubic structure was obtained after a total time of calcination of 8 days, compared to 5 days as necessary for an identical sample synthesized from commercial zirconia. The cell parameters obtained for the yttria cubic-stabilized zirconia samples with chemical formula $(Zr_{0.7}Y_{0.3})O_{1.85}$ are: $a = 0.5166$ nm (YSZ), 0.5164 nm (YSZ-ZRY-4) and 0.5164 nm (YSZ-M5). No trace of SnO$_2$ or niobium oxide was detected in the cubic phase. A similar approach was applied to transform the oxidized claddings of Zircaloy-4 and M5, in comparison to commercial zirconia, into a zirconate pyrochlore Nd$_2$Zr$_2$O$_7$. The neodymium was used as surrogate for An^{3+} (An = Pu, Am, Cm). X-ray diffraction analyses showed the typical pyrochlore structure, with the cell parameters $a = 1.0680$ nm (Py-ZrO$_2$), 1.0675 nm (Py-ZRY-4) and 1.0677 nm (Py-M5).

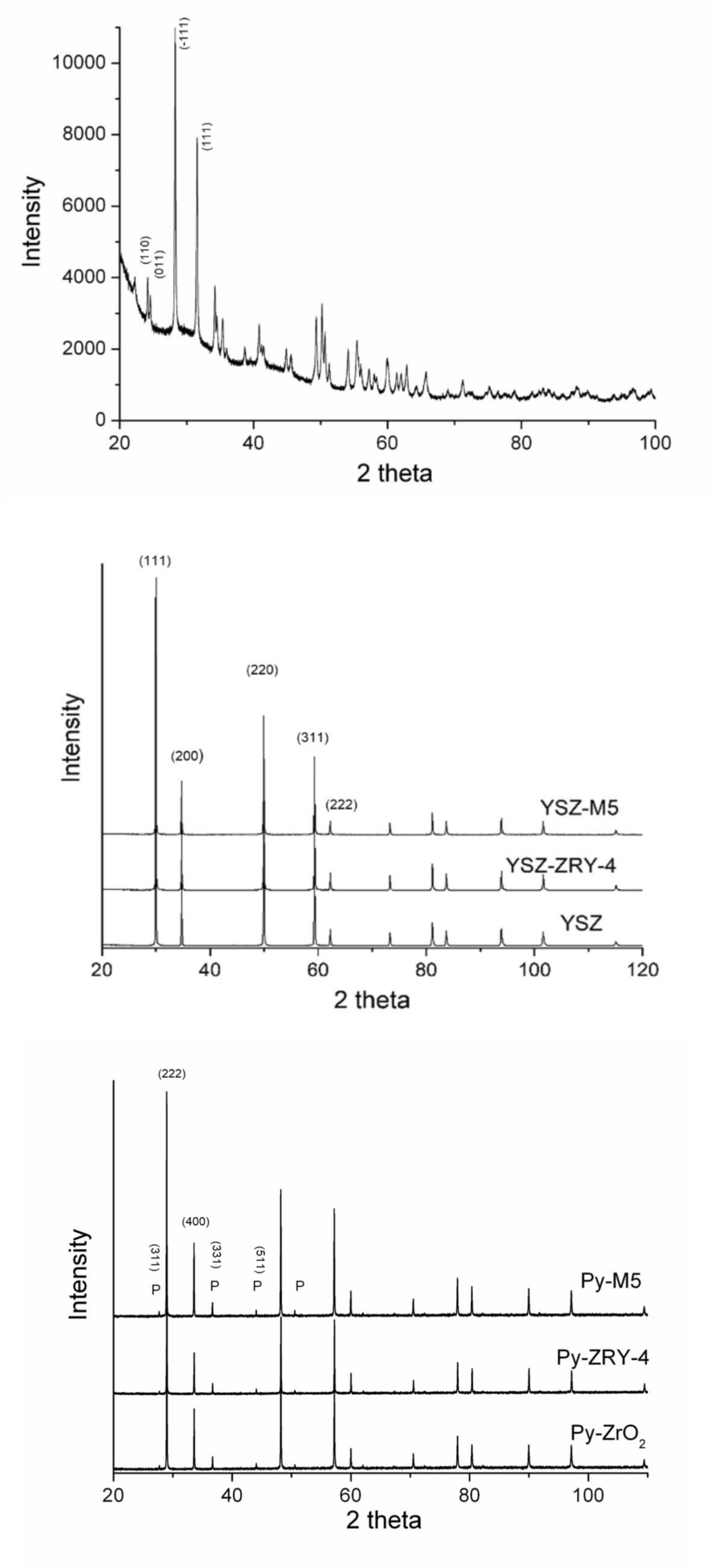

Fig. 3 XRD diffractogram of irradiated Zircaloy-4 after oxidation at 1300 °C for 5 h in air. Monoclinic (top). Comparison of X-ray diffraction patterns of yttria cubic-stabilized zirconia with the composition $(Zr_{0.7}Y_{0.3})O_{1.85}$, obtained from the commercial zirconia, and oxidized Zircaloy-4 and M5 alloys (middle). X-ray diffraction pattern of cubic pyrochlore oxide $Nd_2Zr_2O_7$ obtained from the commercial zirconia, and oxidized Zry-4 and M5 alloys (bottom). The peaks noted P refers to the superstructure of pyrochlores compounds [8]

The small deviation from the theoretical cell parameter for YSZ and pyrochlore $Nd_2Zr_2O_7$ samples could be attributed to the small number of alloying elements contained in the cladding. The ionic sizes in eightfold coordination are as follows: $Zr^{4+}=0.084$ nm, $Sn^{4+}=0.081$ nm, $Nb^{5+}=0.074$ nm, $Y^{3+}=0.1019$ nm [25].

In these preliminary studies we could demonstrate that un-irradiated LWR claddings, either Zircaloy-4 or M5, can be transformed into YSZ and zirconate pyrochlore. The next step of this work will consist of validating these initial data with irradiated cladding. Indeed, during irradiation the cladding suffers several modifications. For instance, it becomes oxidized at its outer surface (100 µm) by reaction with the cooling water along with formation of zirconium hydrides. A thin layer of oxide also forms at the inner surface (10 µm) by reaction with oxygen released from the fuel during irradiation. This inner layer of zirconia contains fission products (FPs) and actinides that have been generated during irradiation. Because zirconia is generally resistant to nitric acid, those FPs and actinides cannot be chemically removed by the standard PUREX process. Various long-lived activation products are also formed in the bulk by neutron capture. The main long-lived isotopes are: ^{93}Zr ($t_{1/2}=1.53\ 10^6$ y), ^{93}Mo ($t_{1/2}=4.0\ 10^3$ y), ^{59}Ni ($t_{1/2}=8.0\ 10^4$ y), ^{63}Ni ($t_{1/2}=10^2$ y), ^{14}C ($t_{1/2}=5.73\ 10^3$ y), ^{36}Cl ($t_{1/2}=3.01\ 10^5$ y). The FPs contained in the cladding represent about 0.15–0.25% in mass and the minor actinides between 0.013 and 0.03% [26] which corresponds to 3.5–15 mg of plutonium per kilogram of zircaloy. Work is now underway in our laboratory to investigate the transformation of irradiated claddings into zirconia-based matrices to evaluate the influence of FPs, actinides on the final product.

Since most FPs, actinides and activation products are strong gamma emitters, irradiated cladding cannot be handled in standard glove boxes in large amounts and their recycling would lead to the necessity of developing novel fuel cycle processes. Their introduction into the fuel fabrication process would require heavier biological shielding than traditional glove boxes. An innovative fuel fabrication process involving pyro-metallurgy in molten salt, instead of the traditional powder metallurgy, could also be envisaged.

To evaluate the amount of cladding that would be needed for such a program, the scenario envisioned, and the stream of actinides produced from reprocessing (e.g., Pu, Pu + Np, Pu + MA, etc.) must be defined.

In the following examples we consider a simple scenario involving either the reprocessing of an UO_2 fuel core, irradiated for 4 years up to 33 GWd/tHM, and initially enriched to 3.5% in ^{235}U or that of a MOX fuel irradiated up to 45.5 GWd/tHM, with an initial content of 5.3% Pu. In the first case, a 900 MWe LWR would produce about 817 kg of plutonium and 72 kg of minor actinides while in the second case, 4800 kg of Pu and 495 kg of minor actinides would be produced. In Table 1 the quantities of actinides that are produced for different type of fuels and burn-ups are compared [27].

A 900 MWe reactor will contain 19.6 metric tons of Zircaloy-4/M5 cladding that will be later converted to 26.5 metric tons of ZrO_2. If one would use the whole amount of zirconia with the whole actinide inventory for the two cases presented in Table 1 (817 + 72 kg) or (4800 + 495 kg), a material with about 1.6 at.% or 9.2 at.% of actinide, respectively $(An_{0.016}Zr_{0.984})O_{2\text{-}x}$ or $(An_{0.092}Zr_{0.908})O_{2\text{-}x}$ would be obtained. This composition is in the range of the plutonium concentration in the IFA-651 irradiation experiment performed in the Halden reactor [28]. If pyrochlore oxides $An_2Zr_2O_7$ are selected, since the tetravalent state of Np cannot be accommodated in this matrix, the actinide inventory to consider for the two scenarios listed in Table 1 would be (817 + 31 + 6 kg) and (4800 + 405 + 77 kg). This would require the use of a lower quantity of irradiated zirconium, approximately 320 kg of Zr in the first scenario and 1984 kg of Zr in the second scenario.

Conclusions

In these preliminary studies we could demonstrate that the un-irradiated LWR cladding, either Zircaloy-4 or M5, can be transformed into yttria-stabilized cubic zirconia $(Zr_{0.7}Y_{0.3})O_{1.85}$ and zirconate pyrochlore $Nd_2Zr_2O_7$. The products formed are single phase which indicates that the other alloying elements, Sn or Nb are incorporated in the final structures. The *reuse* of cladding elements as precursor materials for burning/transmutation and conditioning of actinides would be extremely valuable in terms of waste minimization. We have shown that the total amount of cladding contained in a 900 MWe reactor could be re-used to burn and dispose of the whole inventory of transuranium elements given in Table 1 which would lead to a concentration of between 1.6 at.% $(An_{0.016}Zr_{0.984})O_{2\text{-}x}$ and 9.2 at.% $(An_{0.092}Zr_{0.908})O_{2\text{-}x}$ of actinide. Further work is needed to develop such an innovative fuel cycle involving the recycling of LWR claddings. The next step of this activity will consist of validating our

Table 1 Quantities of actinides that are produced for different type of fuels and burn-ups

84 t. HM (4 years after discharge)	UO_2 3.5% ^{235}U 33 GWd/tHM (kg)	$(U_{0.947}Pu_{0.053})O_2$ 33 GWd/tHM (kg)	$(U_{0.947}Pu_{0.053})O_2$ 43.5 GWd/tHM (kg)
Pu	817	3225	4800
Np	35	12	13
Am	31	243	405
Cm	6	42	77

first testing with irradiated cladding. One particular aspect is to verify if fission and irradiation products can also be incorporated into these lattices in the same way as the Sn and Nb alloying elements.

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Author contributions Conceptualization: PER; Methodology: PER, CCP, MS, TW; Formal analysis and investigation: CCP, MS, TW; Resources: PER, TW; Writing—Original draft: PER; Writing—Review and editing: PER, CCP, MS, TW; Funding acquisition: PER; Supervision: PER; Project administration: PER.

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Data availability The data that support the findings of this study are available upon reasonable request.

Declarations

Conflict of interests The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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